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The investigation on preparation & physicochemical process of nanosized hydroxyapatite powder

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Abstract

The investigations of the preparation and physicochemical process of the HA nanostructured powder with high performance have been performed at present study. The HA preparation starts from the ethanol solution of calcium nitrate tetra-hydrate and phosphorous pentoxide as raw materials. The characterization of the effects of reacting temperatures on preparation, the crystalline degrees (some amorphous HA formed at certain condition) of the reacting products are carried out in the meanwhile. The physicochemical processes and the conditions for different reactions stages of the HA preparation have been traced and characterized by the TG-DTA (thermogravimetric and differential thermal analysis), the FTIR (Fourier-transformed infrared spectroscopy) and other methods. The investigations of the chemical reactions for the HA preparation show that the synthesis of HA is completely finished at the temperature of 500 for hours. The grain sizes and shapes of the HA reacting products are observed and characterized by the TEM and the XRD. The results show that the mean diameters of these product grains are as fine as 30-40nm at the temperature of 500 . The XRD pattern of the present HA powders sintered at 500 for 2h coincided very well with the JCPDS standards showing its superior purity and therefore, with really high performance for later applications.

1. Introduction

Hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, commonly referred to as HA or Hap, has attracted widespread interest because of its excellent biocompatibility and bioactivity. Being the major inorganic constituent of bone HA can provide a chemical bond to the bone and gradually replaced by bone. Hence, HA has become an attractive materials for hard tissue implants[1].

Conventionally, HA powers can be prepared by several methods such as wet precipitation method[2], dry method[3], hydrothermal method[4], sol-gel method[5-12], etc.

The advantages of sol-gel technique include: increase of the homogeneity due to mixing the reagents on the molecular scale; decrease of the heating temperature due to small particle size with high surface areas; ability to produce uniform fine-grained structures.

Various processes and reagents have been used to prepare the HA powder and coating. Pierre[5,6] et al. use calcium diethoxide($Ca(OEt)_2$) and orthophosphoric acid(H_3PO_4)as the reagents. Masuda[7] et al. and Chai CS et al.[8] have prepared HA coating using Calcium diethoxide ($Ca(OEt)_2$) and triethyl phosphate ($PO(OEt)_3$). CM.Lopatin[9] et al. form the sol with a hydrated solution of N-butyl acid phosphate and calcium nitrate tetrahydrate dissolved in 2-methoxyethanol. The reagents such as calcium diethoxide and triethyl phosphate are expensive. It is necessary to find the cheaper reagents in order to produce nanosized HA powder in large quantities. Wenjian Weng[10-11] has ever used the ethanol solution of calcium nitrate tetrahydrate and phosphorus pentoxide to prepare the HA coating on the different substrate. The reagents are cheap but the process is complex because the mixed ethanol

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solution of calcium nitrate tetrahydrate and phosphorus pentoxide need to be refluxed for 24h.

The aim of this paper is to prepare the nanosized HA powders with the cheap reactant and simple process. The results would try to illustrate the physicochemical process of HA preparation with ethanol solution of calcium nitrate tetrahydrate and phosphorous pentoxide.

2. Experimental procedures

Reagent grade $Ca(NO_3)_2 \cdot 4H_2O$ and P_2O_5 are dissolved in ethanol solution according to Ca/P=1.67 respectively. The ethanol solution of P_2O_5 is slowly dropped into the stirred $Ca(NO_3)_2 \cdot 4H_2O$ ethanol solution and then the mixture turn into transparent sol after being continuously stirred for 10min. The mixture is dried at 80℃ for 24h and turns yellow powder. Afterwards, it is ground into powder with a mortar and pestle. The powder is divided into three groups. The first group is used to perform the TG-DTA test with the heating rate of 10℃/min from room temperature to 1300℃. The second group is used to perform the FTIR test. After getting the results of TG-DTA, the exothermic and endothermic peaks and their corresponding temperatures are obtained. In order to investigate the components of the powder, the second group is sintered on Nicolet Magna 750 spectrometer with the heating rate of 10℃ /min. The FTIR spectra are obtained in situ at temperature to which the main exothermic and endothermic peaks respond. The last group is sintered at different temperature and cooled to room temperature to be characterized by XRD patterns(Model: D/max, Japan). Data are collected over 2θ range from 20° to 60°. Identification of phases is carried out by comparing the diffraction data with JCPDS standards. The morphology and size are obtained by TEM(Model: H800, Japan). The sample is dispersed by ultrasound in ethanol for 5min and then deposit on a copper grid for transmission electron microscopic observation. The crystal size is estimated from micrograph.

3.Results and discussion

3.1. TG-DTA results

Fig.1 is the TG-DTA curves of the mixture. The TG curve includes two stages: in the first stage (0—600℃), the weight decrease quickly and about total 64.92% weight loss is observed. weight loss is possibly due to evaporation of water and ethanol and burn of the residual solvent. In the second stage(600-1400℃), the weight decreases slowly and a total weight loss of is just only 3.83%.

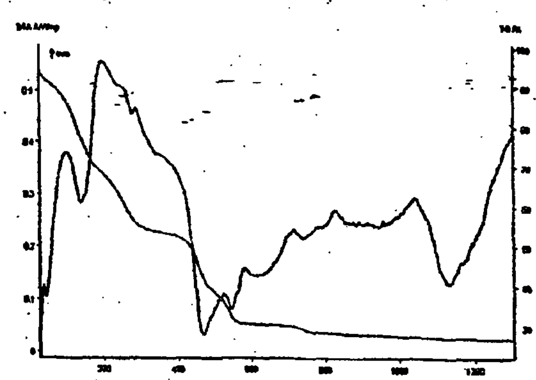

Figure 1 TG-DTA curve of the HA powders

The results of DTA are consistent with those of TG. The DTA curve shows that there are about four exothermic peaks situated at 102.1,195.3,825.8,1047.8℃. The exothermic peaks at 102.1,195.3℃ are due to burn of organic. The exothermic peaks at 825.8,1047.8℃ indicate the onset of crystallization. There are also six endothermic peaks situated at 49,151,273.9,463.3,545,741.7,1138.9℃. The endothermic peaks at about 49,151,273.9,463.3,545℃ are attributed to the evaporation of free water and ethanol or loss of structural water. The endothermic peak at 1138.9℃ possibly shows that the HA decompose into β-TCP and CaO. The HA prepared by wet precipitation method began to decompose at about 1300-1400℃ the temperature of decomposition of HA prepared by sol-gel method is only 1138.9℃ due to the small size and big surface area of grains[10].

3.2 *IR results*

In order to investigate the composition of the mixture at 80,102,151,195,273,350,463℃(the main several exothermic and endothermic peaks are present at these temperature in TG-DTA curves), the IR spectra of the mixture sintered at different temperature are obtained in situ. The results are shown in Figure 2 (a),(b),(c),(d),(e),(f),(g), respectively.

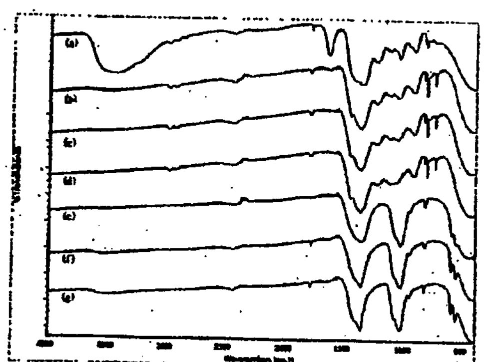

Figure 2 FTIR curve of HA samples heated at different temperatures

In Figure 2, the bands at about 1363 and 835 cm^{-1} are attributed to the NO_3^- ions. In Figure 2 (a), the strong peaks at 3458 and 1637cm^{-1} are attributed to water from ethanol or $Ca(NO_3)_2 \cdot 4H_2O$. In Figure 2 (a),(b),(c),(d), the peaks at about 1236,1064,920,813,742 cm^{-1} assigned to $PO(OH)_{3-x}(OR)_x$[13] are present, suggesting that the mixture is mainly composed of $Ca(NO_3)_2$ and $PO(OH)_{3-x}(OR)_x$ from 80 to 195℃. In Figure 2 (e),(f),(g), the bands at about 1031,1060, 603,563 cm^{-1} are assigned to PO_4^{3-}, indicating the mixture maybe mainly consists of HA, $Ca(NO_3)_2$ and β-$Ca_2P_2O_7$.

It can be seen from Figure 2 that the shapes of (a),(b),(c),(d) are similar and the shapes of (e),(f),(g) are also similar. But the shapes of the two groups are obviously different. On one hand, the peaks at about 1236,1064,920,813,742 cm^{-1}, present in Figure 2 (a),(b),(c),(d), disappear from Figure 2 (e),(f),(g), indicating that $PO(OH)_{3-x}(OR)_x$ decomposes before 273℃. On the other hand, the intensity of peaks at about 1031 cm^{-1} turn stronger in Figure 2 from (a) to (b), suggesting that the amount of HA increases with the elevated temperature. These results are consistent with the following results of XRD patterns.

3.3 *XRD results*

Fig.3(a),(b),(c),(d),(e),(f),(g) are the XRD patterns of mixture sintered at 200,300,400,500,800 and 1200℃.

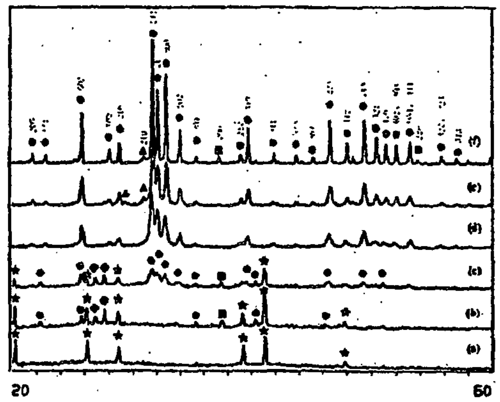

Figure 3 The as-prepared powders heated at different temperature for 2h

(a) 200℃ (b) 300℃ (c) 400℃ (a) 500℃ (b) 800℃ (c) 1200℃

● --HA, ★ – Ca $(NO_3)_2$, ◆ – α-$Ca_2P_2O_7$, ▲ – β-TCP, ■ --CaO

At 200℃, the mixture consists of $Ca(NO_3)_2$ and a small amount of amorphous matter(according to IR analysis, this kind of organic matter is $PO(OH)_{3-x}(OR)_x$). At 300℃ and 400℃, the peaks of HA and CaO is present. This shows that the mixture is composed of $Ca(NO_3)_2$, α-$Ca_2P_2O_7$, HA and CaO. In addition, it can be seen that the amount of HA increase while the amount of $Ca(NO_3)_2$ decrease with the increase of temperature. At 500℃, the peaks attributed to $Ca(NO_3)_2$ and α-$Ca_2P_2O_7$ disappear completely. The XRD patterns are identical to HA. The results in table 1 also showed that sample sintered at 500℃ for 2h is pure HA compared with the JCPDS standards (JCPDS#9-432). The XRD patterns at 800℃ and 1200℃ are similar with the pattern at 500℃. The slight differences are that XRD pattern of HA powders sintered at 500℃ exhibit broad peaks and turned sharper at 800℃ and 1200℃, proving that HA crystallize gradually with the increase of temperature. Additionally, a trace amount of β-TCP(β-$Ca_3(PO_4)_2$) and CaO are detected in the pattern at 800 and 1200℃

Table 1. Comparison of HA samples values heated

at 500℃ for 2h with the JCPDS standards(#9-432)

number	Observed		JSPDS(#9-432)		hkl
	D(Å)	intensity	D (Å)	intensity	
1	2.815	100	2.814	100	211
2	2.719	66	2.720	60	300
3	2.778	59	2.778	60	112
4	3.443	39	3.44	40	002
5	1.839	39	1.841	40	213
6	1.943	37	1.943	30	222
7	2.627	26	2.631	25	202
8	2.263	27	2.262	20	310
9	3.081	16	3.08	18	210
10	1.890	17	1.890	16	212

When the ethanol solution of calcium nitrate tetrahydrate and phosphorus pentoxide are mixed together. The reactions are as follows[1]:

$$P_2O_5+3H_2O \longrightarrow 2H_3PO_4 \quad (1)$$

$$(3-X)C_2H_5OH+H_3PO_4 \longrightarrow PO(OH)_X(OC_2H_5)_{3-X}+(3-X)H_2O \quad (2)$$

$$Ca(NO_3)_2 + 2C_2H_5OH \longrightarrow Ca(C_2H_5O)_2 + 2HNO_3 \quad (3)$$

$$Ca(NO_3)_2 + H_3PO_4 \longrightarrow CaHPO_4 + HNO_3 \quad (4)$$

From 200 to 500, The process can be described as Eq. (5),(6),(7),(8)[6]:

$$2CaHPO_4 \longrightarrow H_2O + Ca_2P_2O_7 \quad (5)$$

$$Ca(OC_2H_5)_2 + H_2O \longrightarrow CaO + 2C_2H_5OH \quad (6)$$

$$3\ Ca_2P_2O_7 + H_2O + 4CaO \longrightarrow Ca_{10}(PO_4)_6(OH)_2 \quad (7)$$

$$10Ca(NO_3)_2 + 6PO(OH)_X(OC_2H_5)_{3-X} + (20-6X)H_2O \longrightarrow Ca_{10}(PO_4)_6(OH)_2 + 6(3-X)C_2H_5OH + 20HNO_3 \quad (8)$$

The results of Figure 3 have proved that the mixture are composed of Ca2P2O7 ,CaO, HA. The amount of HA increases with the increase of temperature. The reactions to prepare HA in Eq. (7),(8) are finished at 500

A amount of HA begins to decompose over 800 as described in Eq. (9)[10] .

$$Ca_{10}(PO_4)_6(OH)_2 \longrightarrow 3Ca_3(PO_4)_2 + CaO + H_2O \quad (9)$$

In short, the results from XRD patterns are consistent with the results of IR analyses and TG-DTA results. The mixture consists of $Ca(NO_3)_2$, HA, $PO(OH)_{3-x}(OR)_x$. α-$Ca_2P_2O_7$ and CaO from 200 to 500℃. At 500℃, mixture is mainly composed of HA. The morphology of the HA powder sintered at 500℃ for 2h is shown in Figure 4. The individual particles are uniform. The size is about as big as 30-40nm. At 800℃,1200℃, the mixture is composed of HA , a trace amount of β-TCP and CaO.

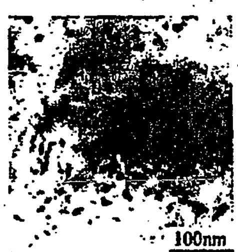

Figure 4 Transmission electron micrograph of HA grains heated at 500℃ for 2h

4.Conclusion

Nanosized HA powders can be prepared from ethanol solution of $Ca(NO_3)_2 \cdot 4H_2O$ and P_2O_5 by sol-gel method. The reactants are cheap and the process is simple without refluxing. The results are encouraging because the advantages offered by this process can make it possible to produce the nanosized HA powder at low cost in large quantities. The size of hydroxyapatite crystal sintered at 500 ℃ for 2h is as fine as about 30-40nm. The synthesis of HA is finished until about 500℃. From 200 to 500℃,The mixture is composed of amorphous HA, $Ca(NO_3)_2$, $PO(OH)_{3-x}(OR)_x$, α-$Ca_2P_2O_7$. A trace amount of β-TCP and CaO are present due to the decomposition of HA after 800℃.

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